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(54) Coated zirconium oxide fibers.

(57) Improved silicon-free zirconia fibers have coated or modified surfaces. Strong, flexible, zirconia fibers can be prepared in a process involving the addition of colloidal ZrO_2 particles to a fiber precursor solution. The zirconia fibers can be coated or their surfaces modified with at least one of a hydrophilic or hydrophobic polymer, a bioactive material, and an inorganic phosphate or an organophosphorus compound. The coated or modified fibers are useful in chromatographic applications.

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Field of the Invention

This invention discloses coated zirconia fibers and a process for their preparation. The coated zirconia fibers are useful in chromatographic and immobilization applications.

Background of the Invention

Chromatographic separations are becoming increasingly important in today's high tech society. The use of porous, spherical ZrO_2 particles for various types of chromatographic stationary phases has been disclosed in U.S. Patents 3,782,075, 4,010,242, and 4,138,336.

Methods of improving the alkaline stability of particulate SiO_2 by cladding the surface with a more base stable metal oxide such as zirconium oxide (ZrO_2) have been disclosed in U.S. Patent Nos. 4,648,975 and 4,600,646. This cladding is disclosed to increase the upper pH limit at which these supports, also referred to as packings, can be used to 11 and 9.5, respectively. However, these packings still lack adequate stability to allow them to be sterilized and cleaned in, for example, 0.1 N aqueous sodium hydroxide (NaOH, pH = 13).

Tubular reactors and chromatography columns having good axial flow characteristics at high packing densities have been made by packing tubes with bundles of continuous glass fibers that are in generally parallel alignment as disclosed in U.S. Patent Nos. 4,657,742 and 4,715,105. Use of cellulosic and organic fibers is suggested in U.S. Patent No. 4,657,742. Use of ceramic fibers is not suggested.

The majority of separations employing high pressure liquid chromatography (HPLC) are performed in the so-called reversed-phase mode. In this mode, the column-packing material is referred to as stationary phase. The most commonly used stationary phases feature a non-polar ligand (e.g., octane or octadecane) covalently-bound to a porous silica particle through a siloxane bond (Si-O-Si) to render the surface hydrophobic. Although these silica-based bonded phases are very useful for a wide range of applications in reversed-phase HPLC, their use is strictly limited to the pH range of between 2 and 8, due to the hydrolytic instability of both the silica support particle and the siloxane bond used to "anchor" the non-polar active group.

Ion-exchange chromatography (IEC) has become an important separation technique for the purification of biomolecules. Typical supports used in IEC are silica, alumina, agarose, polymethacrylate, and poly-(styrene-divinylbenzene). See H. G. Barth et al., Anal. Chem., 60, 387R (1988). Agarose is not suitable for high pressure work, while silica and alumina have limited pH stability. The matrices of silica and alumina must also be derivatized or coated to provide the support with ion exchange properties. This often introduces hydrophobic interactions into the retention mechanism. The hydrophobic nature of hydrocarbon-based supports such as poly(styrene-divinylbenzene) must be masked in order for them to be used as IEC supports. The hydrocarbon-based supports are also subject to shrinking and swelling whereas inorganic supports are not.

Zirconium phosphate has been extensively studied as an inorganic ion exchanger for the nuclear industry because of its excellent exchange capacities, radiation and thermal stability. See A. Clearfield et al., Ion Exchange and Solvent Extraction, J. A. Marinsky et al., eds., Marcel Decker, New York, (1973) at Chapter 1. However, relatively little work has been done using zirconium phosphate as an HPLC support because of its poor mechanical properties and the lack of materials with the necessary porous structure. Furthermore, zirconium phosphate lacks the mechanical stability necessary for high performance chromatographic supports.

Summary of the Invention

Briefly, the present invention discloses fired ZrO_2 fibers coated in such a manner as to make them useful in reverse phase, ion exchange, and size exclusion chromatography applications. In these applications fibers with high surface areas are preferred.

Preferred zirconia fibers useful in the present invention are disclosed in U.S. Patent No. 4,937,212 and are continuous, silicon-free, carbon-free, zirconia fibers having a diameter greater than 5 micrometers, preferably in the range of 8 to 25 micrometers and having a tensile strength greater than 0.5 GPa, preferably in the range of 1.0 to 5.0 GPa, and most preferably greater than 2.0 GPa.

A process for the preparation of strong, flexible, zirconium oxide based fibers of diameters from 0.5 to 60 micrometers is also disclosed in U.S. Patent No. 4,937,212. The fibers may be either continuous or discontinuous in form and may possess either high surface area (in the range of 1 to 200 m^2/g, and having an average pore size in the range of 20 to 500A, preferably 100-300A) or low surface are (less than 1 m^2/g)

depending on the processing conditions employed. The process for their preparation involves incorporation of crystalline colloidal ZrO_2 particles into the fiber precursor also containing a soluble zirconium compound and a solvent. The presence of these colloidal particles allows strong, continuous fibers with larger diameters than previously achievable to be prepared.

As used in the present application, "zirconia fibers" means fibers consisting of crystalline zirconia which may also contain other metal oxides as phase change stabilizers, grain growth inhibitors, or catalytic materials. By silicon-free is meant not containing silicon other than as an impurity at a level of less than about 2 weight percent.

Detailed Description of Preferred Embodiments

The present invention provides, in a preferred embodiment, zirconia fibers and a method for preparing a ceramic fiber. The present invention also provides ceramic fibers which are coated with a continuous or discontinuous layer of a crosslinked hydrophobic or hydrophilic polymer. For enhanced utility in certain applications, the fiber can be modified with an effective amount of an inorganic phosphate or with an organophosphorus compound such as an organophosphonate or organophosphonic acid, prior to or following application of the hydrophobic polymer. Bioactive materials can be sorbed onto the exterior or interior surfaces of both the uncoated and polymer-coated fibers. Coated fibers of the invention, in continuous or discontinuous form, are useful in reverse phase, ion exchange, and size exclusion chromatography applications. In preferred embodiments, the ceramic zirconia fibers coated as just described with a hydrophobic polymer can be used to produce chromatography column support material, such as for use in high-performance liquid chromatography (HPLC), which resists dissolution and is therefore stable in aqueous media over a wide pH range. Zirconia fibers, when treated with a hydrophilic crosslinked polymer, can provide an ion-exchange support material. Coated fibers of the invention are stable in aqueous solutions of pH in the range of 1 to 14.

Preferred zirconia fibers and a method therefor for use in the present invention are disclosed in U.S. Patent No. 4,937,212. The zirconia fibers comprise crystalline zirconia grains having a grain size of at most 1.0 micrometer, the fiber having a diameter in the range of 5 to 50 micrometers and a tensile strength greater than 0.5 GPa.

The coated ZrO_2 fibers of the present invention which are useful in chromatographic applications have coatings on, or modifications to, the fiber surface which impart the desired surface chemistry. Coated fibers have diameters in the range of 0.5 to 100 micrometers, preferably 5 to 80 micrometers, and more preferably 10 to 60 micrometers. Materials for and methods of coating ZrO_2 spherules so as to produce reverse phase, ion exchange, and size exclusion supports are disclosed in applicant's co-pending application U.S. Serial No. 07/151,819, filed 2/3/88 and in its CIP, U.S. Serial No. 07/420,150, filed 10/11/89, which applications are incorporated herein by reference for their teachings of coatings and methods of providing coatings on a zirconia support. The coated fibers of the present invention are particularly useful in continuous form when employed as the packing material for an alligned fiber chromatography column.

The coated fibers are prepared by adsorbing a polymerizable monomer or oligomer onto the surface of the fibers as by, for example, solution infiltration processes such as dipping (preferably under vacuum), or any other coating means known in the art and subsequently cross-linking it, e.g., by reaction of the adsorbed material with a free radical initiator or by irradiation. The polymeric coating renders the ZrO_2 fibers hydrophobic without substantially altering any of their desirable physical and mechanical properties. Likewise, the ZrO_2 fibers can be coated with a hydrophilic, cross-linked polymer having exchangeable groups to form an ion-exchange support material. Coating thicknesses can be in a range greater than zero and up to 20 micrometers, preferably about 0.0001 to 5.0 micrometers, more preferably 0.0001 to 0.1 micrometers. ZrO_2 fibers having surface areas in the range of 1 to 200 m^2/g (highly porous) are preferred.

The coated fibers can also be combined with a suitable binder and used to coat a glass or plastic substrate to form plates for thin-layer chromatography.

In a preferred embodiment, the present invention is directed to a chromatographic support material comprising porous ZrO_2 fibers having a surface modification or a cross-linked polymeric coating thereon, wherein said coated fibers are hydrophobic, the modified or coated fibers having a pore size from about 20-500 A and an average diameter of about 0.5-100 micrometers.

The ZrO_2 fibers of the present invention can also be employed to immobilize bioactive materials for a variety of purposes, including catalysts, analysis, affinity chromatography and synthetic transformations. Bioactive materials can be strongly sorbed onto the exterior and interior surfaces (pores) of uncoated, polymer-coated, and inorganic phosphate or organophosphorus compound surface-modified ZrO_2 fibers, while retaining a large percentage of their initial bioactivity. Representative biomaterials include proteins

such as enzymes and antibodies.

In another embodiment, coated or uncoated ZrO_2 fibers can be prepared which comprise a biologically active material such as an enzyme or a protein such as an immunoglobulin. Upon depletion of the biological activity, the enzyme or other protein can be removed from the fibers by exposing them to an aqueous medium at high pH, e.g., by washing them with a solution of an alkali metal hydroxide. The fibers, stripped of the biological materials, can then be treated with a buffer to return them to a physiological pH, and subsequently reloaded with the same, or a different bioactive material.

The coated ZrO_2 fibers may also be exposed in situ to traditional sterilization conditions, for example, by exposing the packing or the packed column to heat and high pH, without significant degradation.

In yet another embodiment of the invention, the surface of the coated or uncoated ZrO_2 fibers is deactivated or modified by treatment with an effective amount of an inorganic phosphate, such as phosphoric acid or an alkali metal phosphate salt, or with an organophosphonate, prior to or following application of the hydrophobic polymer coating. The treatment conditions can be varied so as to either reversibly adsorb phosphate, which may be phosphate ion, onto the ZrO_2 surface, or to bind the phosphate onto and/or into the ZrO_2 surface, for example, as zirconium phosphate. These treatments render the fibers effective to separate negatively charged molecules such as sulfonates, carboxylates, and other oxyanions. It is also believed that the organophosphonate becomes incorporated into the organic matrix of the polymeric coating.

The majority of HPLC methodology employs the so-called "reverse phase" mode, i.e., the column-packing material (stationary phase) is non-polar and the eluent (mobile phase) is polar. Therefore, it is preferred to coat the surface of the ZrO_2 fibers with a hydrophobic coating, which is also preferably stable to aqueous solutions having a pH of about 1-14. Hydrophilic polymer coatings can also be applied and cross-linked for modification of the ZrO_2 fibers to form an ion exchange support or a steric exclusion support. These hydrophilic polymer coatings are formed from monomers or oligomers which comprise polar groups such as sulfonic acids, carboxylic acids, amino groups, hydroxyl groups, amido groups or quaternary ammonium groups. A preferred method to prepare such a coating comprises sorbing a polymerizable monomer or oligomer onto the surface of the fibers, and cross-linking the monomer or oligomer. See G. Shomberg, LC-GC, 6, 36 (1988).

Polymerizable Monomers or Oligomers

A wide variety of cross-linkable organic materials, which may be monomers, oligomers or polymers, can be employed to coat the porous ZrO_2 fibers. For example, such materials include polybutadienes, polystyrenes, polyacrylates, polyvinylpyrrolidones (PVP), polyvinyl alcohols (PVA), polyorganosiloxanes, polyethylenes, poly(t-butyl)styrenes, polyisoprenes, polyethyleneimines, polyaspartic acids and multifunctional silanes.

A preferred material for the preparation of a reversed phase support material is an oligomer of polybutadiene. A preferred material for modification of the ZrO_2 fibers to form a cation ion exchange support is polyaspartic acid. A preferred material for construction of a support suitable for aqueous steric exclusion chromatography is a tri- or di-alkoxy-,gamma-glycidoxy silane.

Cross-linking Agents

Any of the common free radical sources including organic peroxides such as dicumyl peroxide, benzoyl peroxide or diazo compounds such as 2,2'-azobisisobutyronitrile (AIBN) may be employed as cross-linking agents for polymer coatings in the practice of the present invention. Useful commercially available peroxyesters include the alkylesters of peroxycarboxylic acids, the alkylesters of monoperoxydicarboxylic acids, the dialkylesters or diperoxydicarboxylic acids, the alkylesters of monoperoxycarbonic acids and the alkylene diesters of peroxycarboxylic acids. These peroxyesters include t-butyl peroctoate, t-butyl perbenzoate, t-butyl peroxyneodecanoate and t-butyl peroxymaleic acid. These compounds are commercially available from Pennwalt Chemicals, Buffalo, N.Y. The amount of any free radical initiator required to catalyze the polymerization reaction will vary depending upon the molecular weight of the initiator and its thermal stability. Oligomers may also be polymerized by thermal treatment, by irradiation with UV light or gamma rays or by exposure to high energy electrons.

A column "fouled" by repeated injections of large amounts of material, to the point that a marked change in characteristics is observed, can be stripped of "irreversibly adsorbed" material. The original column performance can be restored by pulsing the column with 100 µl injection of 1 M NaOH or by flushing the column for about 0.5-10 hrs with aqueous alkali metal hydroxide, i.e., with a 0.1 M NaOH

solution.

Bioactive Materials

A wide variety of bioactive materials can be bound to the uncoated or polymer-coated fibers by presently-available techniques so that their bioactivity is retained and prolonged, or "stabilized" with respect to the unbound bioactive material. For example, antibodies or enzymes can be bound to the uncoated fibers in high concentrations by agitating an aqueous mixture of degassed fibers and antibody in a buffer, e.g., for about 0.1-5 hrs under ambient conditions. For a review of other noncovalent and covalent enzyme-binding methodologies, see R. A. Messing (U.S. Patent No. 3,850,751), the disclosure of which is incorporated by reference herein.

Enzymes capable of being bound and stabilized as described herein include a wide variety of enzymes which may be classified under six general groups: hydrolytic enzymes, redox enzymes, transferase enzymes, lyases, isomerases and ligases. The first group, hydrolase enzymes include proteolytic enzymes which hydrolyze proteins, e.g., papain, ficin, pepsin, trypsin, chymotrypsin, bromelin, keratinase, carbohydrases which hydrolyze carbohydrates, e.g., cellulase, glucuronidase, amylase, maltase, pectinase, chitinase; esterases which hydrolyze esters; e.g., lipase, cholinesterase, lecithinase, phosphatase; nucleases which hydrolyze nucleic acid, e.g., ribonuclease, deoxyribonuclease; and amidases which hydrolyze amines, e.g., arginase, asparaginase, glutaminase, and urease. The second group are redox enzymes tht catalyze oxidation or reduction reactions. These include glucose oxidase, catalase, peroxidase, lipoxidase, and cytochromes. The third group are transferase enzymes that transfer groups from one molecule to another. Examples of these are glutamic-pyruvic transaminase, glutamic-oxalacetic transaminase, transmethylase, phosphopyruvic transphosphorylase and dehydrogenase. The fourth group are lyase enzymes tht catalyze the cleavage of C-C, C-O, C-N and other bonds by elimination, leaving double bonds, or conversely, adding groups to double bonds. Examples of these are pyruvate decarboxylase, amino acid decarboxylases, aldolase, fumarate hydratases, aconitate hydratases and ammonia lyase. The fifth group are isomerase enzymes that catalyze the dehydrogenation and epimerization of amino acids and sugars. An example of an isomerase is phosphoglucomutase. The sixth group are ligase enzymes that catalyze the synthetic linking of two molecules, simultaneously with the breakdown of ATP. Examples of these are aminoacyl-tRNA synthetases and biotinyl-dependent carboxylases.

Other proteins capable of being bound and stabilized as described herein include Concanavalin-A, Protein-A, acid glycoproteins, plasma immunoglobulins, monoclonal antibodies, bioactive polypeptides such as serum proteins and immunomodulators, e.g., lymphokines and the like. Other examples of proteins which are bound by the present fibers are provided in the working example hereinbelow.

Phosphate Modification

The surface of uncoated or polymer-coated ZrO_2 fibers can be easily and dramatically modified in a chromatographically-beneficial way by treatment with aqueous inorganic phosphate solutions. The combination of polymer coating and phosphate treatment in either order produces a mixed mode stationary phase exhibiting both cation-exchange and reversed-phase properties. This allows one to adjust the selectivity of the present support material with respect to a group of basic solutes by appropriate adjustment of mobile phase pH, ionic strength, and reversed-phase eluting strength (i.e., volume fraction of the adjuvant organic solvent).

Useful aqueous inorganic phosphate solutions include about 0.01-1.0 M solutions of phosphoric acid (H_3PO_4) or of alkali metal phosphate salts, e.g., orthophosphates, pyrophosphates, metaphosphates, tripolyphosphates and the like.

Although phosphate ions can be adsorbed onto the ZrO_2 surface by exposure to dilute (0.01-0.5 M) aqueous solutions of various inorganic phosphates for relatively short periods of time (e.g., 1-3 hours) at ambient temperatures (20-30° C), the phosphate is slowly removed from the surface under conditions of high pH. Therefore, it is preferred to treat the surface of the ZrO_2 fibers with relatively concentrated (0.05-1.0 M) aqueous solutions of inorganic phosphates for longer periods of time (three or more hours) and/or at elevated temperatures (e.g., 90-110° C), so that the phosphate ions react with and become incorporated into an outer layer of the fiber, for example, as, e.g., zironium phosphate. Preferably, the treated fibers will comprise about 0.5-15.0 wt-% phosphate.

This phosphate incorporated into the structure as zirconium phosphate is less readily removed by hydrolysis reactions than the surface adsorbed phosphate ions are by exchange processes. Both of these types of phosphate groups will nevertheless be gradually lost upon exposure to conditions of high pH (>10)

in flowing mobile phases. This loss of phosphate can be reduced by keeping phosphate present in the mobile phase. Additionally, it is also possible to recondition a column which has lost phosphate by exposing it to phosphating conditions.

It is important to note that the underlying ZrO_2 fibers remain stable. It is therefore possible to perform an ion exchange separation with a column packed with phosphate-coated fibers, clean the column by flushing with strong base, and if necessary expose the column to phosphating conditions prior to the next separation operation. These cycles may be repeated indefinitely.

For purposes of calculating wt-% phosphate in the treated fibers, it will be assumed that each phosphate ion incorporated into the ZrO_2 fiber possesses four oxygen atoms. The weight percentage of phosphate can thus be calculated from a knowledge of the weight percentage of phosphorus in the fiber by the following formula:

$$\text{wt-\% phosphate} = \text{wt-\% phosphorus} \times \frac{95\ [\text{molecular wt. } PO_4]}{31\ [\text{atomic wt. P}]}$$

The weight percentage of phosphorus in the fibers can be measured by inductively coupled plasma spectroscopy (ICP). The amount of phosphorus incorporated in the fibers for a given exposure condition is directly related to the specific surface area of the ZrO_2 fiber.

For example, treatment of the ZrO_2 fibers having a specific surface area of about 117 m^2/g for about 1-4 hours at about 25° C with an excess of an aqueous solution of phosphoric acid with a concentration from about 0.01-1.0 molal yields fibers containing about 2.0-5.0 wt-% phosphate. Treatment of ZrO_2 fibers for about 1-4 hours at about 100° C with an excess of about 0.01-1.0 molal H_3PO_4 yields fibers containing about 2.0-12.0 wt-% phosphate.

Although not intending to be bound by any particular theory of action, it is believed that these more rigorous treatment conditions, including temperatures of about 90-110° C, cause the phosphate ions to chemically react with and be incorporaed into the ZrO_2 fibers. Thus, the outer surfaces (both external and internal) of the fibers are at least partially converted to zironium phosphate. The thickness of this zirconium phosphate layer is governed by the reaction conditions employed. High phosphate concentrations, higher temperatures and longer reaction times lead to the formation of thicker layers. These fibers exhibit desirable cation exchange properties, while retaining the high mechanical and pH stability exhibited by untreated fibers. As discussed above, while less stable at elevated pHs and temperatures than the underlying ZrO_2 fibers, the phosphate coatings possess useful stabilities and can be readily regenerated by exposure to solution sources of inorganic phosphate.

Modification with Organophosphorus Compounds

For some applications, it is desirable to further deactivate or modify the surface of the uncoated or polymer-coated ZrO_2 fibers. This can be accomplished by treating the uncoated ZrO_2 fibers with an organophosphorus compound in a suitable solvent for the organophosphorus compound. Preferred organophosphorus compounds include the saturated or unsaturated organophosphonic acids and the water-soluble salts thereof, e.g. the alkali metal salts. Useful organophosphorus compounds include organophosphonates such as allylphosphonates, octyl phosphonates, diallyl phosphorates, allylphosphonic acid, phenyl phosphonic acid, naphthyl phosphonic acid, phenyl phosphinic acid, phenylphosphoric acid, and the salts thereof.

Useful solvents for the organophosphorus compound include aqueous alcohol, e.g., a solution of water and a (C_1-C_5) alkanol. The ZrO_2 fibers are preferably coated by agitating the fibers in a solution of the organophosphorus compound so that the weight ratio of the organophosphorus compound to fibers is about 0.25-1:1. The treated fibers are then separated from the treating solution, and dried. The cross-linked polymeric coating then can be applied as disclosed hereinabove.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention.

Testing Methods

The surface areas of the fibers were determined by the Brunauer-Emmett-Teller (BET) nitrogen adsorption technique using a Quantasorb™, Model SW-6 surface area measuring instrument (commercially available from Quantachrome Corp., Syosset, New York).

Tensile strength data were obtained by the application of load on a single filament. For most measurements a gauge length of 12.8 mm was used. For some measurements of weaker fibers a 6.4 mm gauge length was used. A uniform loading rate of 120 g per minute was used. To enable the calculation of tensile strength, filament diameters were measured directly using a micrometer.

Modulus of elasticity data were obtained on single fibers using a vibration resonance technique. A short (1 to 2 cm) length of fiber was glued onto a metal substrate attached to an accoustical driver so that it was cantilevered out from the substrate perpendicular to the direction of vibration. When the accoustical driver was oscillated, the fiber had several distinct and unique frequencies of resonance, the patterns of which were observed with a binocular microscope. The dynamic elastic modulus of the fiber was calculated according to the following equation:

$$E = 64\Pi^2 p(LF/dk)^2$$

where E = elastic modulus, L = fiber length, d = fiber diameter, F = resonant frequency, k = mode coefficient, and p = fiber density.

For calculation of elastic modulus, the fiber density was assumed to be 6.1 g/cm^3. The viscosities recited are Brookfield viscosities measured at ambient room temperature. In describing a fiber as "transparent", this term means that the fiber when viewed under an optical microscope, e.g., with a stereoscopic microscope at 50X and oblique or transmitted light, has the property of transmitting rays of visible light. Thus, bodies beneath and contiguous with the transparent fiber, such as fibers of the same nature, can be clearly seen therethrough, the outline, periphery or edges of contiguous bodies beneath being sharply discernible. "Opaque" fibers, on the other hand, as referred to herein are those which are impervious to visible light, i.e., contiguous bodies beneath are obscured by opaque fibers and cannot be seen therethrough. "Translucent" fibers are those whose ability to transmit light falls between transparent and opaque, and although translucent fibers have the property of transmitting visible light to some degree, and therefore are somewhat or partially transparent, contiguous bodies beneath can be seen in a diffuse manner rather than in a clearly distinguishable or sharp manner.

Sometimes, because of vagaries in firing, a fiber product may be a mixture of these various types of fibers (viz., transparent, opaque, translucent) though generally one type will be present in a predominant amount, indicative of the true nature of the mixture, the other types of products present in minor amounts having their particular appearance due to incomplete firing at the desired temperature or due to overheating because of hot spots in the furnace.

The practice of the present invention is illustrated by, but not limited to the following examples.

Example 1

This example describes the preparation of highly porous, continuous, ZrO_2 fibers for coating in the subsequent examples. To 200 g of Nyacol Zr 100/20 colloidal zirconia sol (containing 20 wt-% ZrO_2) was added 3 g of concentrated nitric acid. To this was added 40 g of zirconyl acetate solution (containing 25 wt-% equivalent ZrO_2) with stirring. 33 g of PVP K-30 (50% aqueous solution) were then added with stirring. The mixture was filtered through a 0.3 micrometers AA Grade cartridge filter into a round bottom flask and concentrated on a rotary evaporated to a viscosity of approximately 100 PaSec. Fibers were extruded and drawn as described in Example 4. The fibers spun well and glossy, transparent, strong, continuous, green fibers were obtained. These green fibers were heated from room temperature to 600° C over 20 hours and then allowed to cool. The fired fibers were continuous and had diameters in the range of 10 to 15 micrometers and had a surface area of about 48 m^2/g. Protein can be immobilized on the surface of the fibers using the procedure of Example 12 of U.S.S.N. 07/420,150, filed 10/11/89.

Example 2

This example describes the coating of a portion of the fibers prepared as described in Example 1 with a polymer, polybutadiene, so as to make their surfaces hydrophobic and therefore useful in reverse phase chromatography applications.

The polybutadiene used was obtained from Aldrich Chemical Corporation and had a stated molecular weight of 4,500 and its double bonds were 45% vinyl and 55% cis and trans - 1,4-polybutadiene. 0.05 g of

this polybutadiene was dissolved in 100 ml of heptane in a 250 ml round bottom flask. .0012 g of dicumyl peroxide were added as a free radical initiator for the polymerization of the polybutadiene. 2.0 g of the fibers prepared as per Example 16 were added to the flask. The flask was then placed on a rotary evaporator and rotated under a vacuum of about 25 inches of Hg for 30 minutes. The vacuum was increased to 27 inches of Hg and the heptane was removed. The polybutadiene coated ZrO_2 fibers were dried in air and then cured at 190° C for 4 hours under vacuum to polymerize the polybutadiene. To remove any uncrosslinked polybutadiene which might be adsorbed to the fibers, the cured fibers were extracted for 4 hours with refluxing heptane in a Soxhlet extractor.

The surface area of the coated, cured, and extracted fibers was 28 m^2/g. The carbon, hydrogen, and nitrogen content of the fibers was determined by analysis to be consistent with the presence of a coating on the surface of a crosslinked layer of polybutadiene. The fibers had a tan color, and remained strong and continuous.

Example 3

This example describes the reaction of the surface of a portion of the fibers prepared in Example 1 with phosphoric acid to prepare a fiber with phosphate incorporated in its surface. These fibers were useful in ion exchange chromatography applications.

1.18 g of concentrated phosphoric acid (85% H_3PO_4) was diluted with enough deionized water to produce a 1 wt-% solution. This solution was placed in a round bottom flask and 1.0 g of the fibers prepared as described in Example 16 was added. The flask was placed on a rotary evaporator and rotated under a vacuum of about 27 inches of Hg for about 30 minutes. The flask was then removed from the rotary evaporator. The flask was placed in a heating mantle and the solution was boiled for 30 minutes. The fibers were then removed from the flask, blotted dry with paper towels, and left to dry in air overnight.

The surface area of the phosphate treated fibers was 47 m^2/g. A portion of the fibers was dissolved in hydrofluoric acid and analyzed for phosphorous content by Inductively Coupled Plasma Spectroscopy. The fibers contained 2.9 wt-% phosphate consistent with the presence of phosphate ions incorporated in the surface of the fibers. The fibers remained strong and continuous.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

Claims

1. A fired ZrO_2 fiber having on its surface at least one of a coating and a surface modification selected from the group consisting of a layer of a cross-linked polymer, an immobilized protein, an inorganic phosphate, and an organophosphorus compound wherein said coated or modified fiber has a diameter in the range of 0.5 to 100 micrometers.

2. The fiber according to claim 1 wherein said fiber is porous and has pore sizes in the range of 20-500 Å.

3. The ZrO_2 fibers according to claims 1 and 2 wherein said layer of surface modification is an organophosphonic acid, or surface-adsorbed inorganic phosphate.

4. The fiber according to claims 1 to 3 which is a cation-exchange material.

5. The fiber according to claims 1 to 4 wherein said inorganic phosphate is derived from phosphoric acid or an alkali metal phosphate salt.

6. A thin layer chromatography plate comprising a substrate coated with a mixture of a binder and fiberous support material comprising fibers according to claims 1 to 5.

7. A bed comprising ZrO_2 fibers according to claims 1 to 6 having diameters in the range of 0.5 to 100 micrometers, 1-200 m^2/g surface area and of 20-500 Å pore diameter.

8. The bed according to claim 7 which comprises an antibody or enzyme immobilized on said fibers.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 30 0762

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	EP-A-0 331 283 (REGENTS OF THE UNIV. OF MINNESOTA) " Page 17; claims 1-18 "	1-8	B 01 J 20/08 B 01 J 39/12 G 01 N 30/48 B 01 J 20/32
A	EP-A-0 328 256 (OWENS-CORNING FIBERGLAS) " Pages 13-14; claims "	1,8	C 01 G 25/02
P,A	FR-A-2 644 449 (NIPPON ELECTRIC GLASS) " Pages 22-23 "	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B 01 J
G 01 N

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	04 June 91	WENDLING J.P.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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E: earlier patent document, but published on, or after the filing date
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